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## (54) PURIFICATION OF HYDROCHLOROFLUOROETHANES

(57) The olefinic impurities are removed from hydrochlorofluoroethanes of formula:  $\text{CF}_3\text{-CHCIX}$  (X = H, F, or Cl) by subjecting the impure hydrochlorofluoroethanes to photochlorination, under UV or visible light radiation of 320 - 500 m.n.

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Although the selectivities of these fluorinations are generally good, the products obtained are nevertheless accompanied by a number of impurities, especially of more or less fluorinated compounds

5 (CF<sub>2</sub>ClCH<sub>2</sub>Cl, CFCl<sub>2</sub>CH<sub>2</sub>Cl, CF<sub>3</sub>CH<sub>2</sub>F, CF<sub>3</sub>CHCl<sub>2</sub>, CF<sub>3</sub>CH<sub>3</sub>), of C<sub>2</sub> olefins such as CF<sub>2</sub>=CHCl, CF<sub>2</sub>=CFCl, CF<sub>2</sub>=CCl<sub>2</sub> and CFCl=CCl<sub>2</sub>, and of C<sub>4</sub> olefins such as CF<sub>3</sub>CH=CHCF<sub>3</sub>, CF<sub>3</sub>CH=CFCF<sub>3</sub>, CF<sub>3</sub>CH=CClCF<sub>3</sub> and CF<sub>3</sub>CF=CClCF<sub>3</sub>.

These impurities are obtained in larger quantities in the gas-phase process and, in particular, when the fluorination is carried out in the presence of oxygen, to stabilize the catalyst activity (Patent EP 583 703). Thus, in the course of fluorination of trichloroethylene (TCE) on a bulk chromium oxide, under

15 the following conditions:

Temperature	: 350°C
Pressure	: 15 bars
Contact time	: 14 seconds
HF/TCE molar ratio	: 10
20 O <sub>2</sub> /TCE molar ratio	: 0.06

an F133a containing approximately 3 % of C<sub>4</sub> olefinic products (essentially CF<sub>3</sub>CH=CHCF<sub>3</sub>) was obtained.

These C<sub>4</sub> impurities are particularly difficult to remove because they have volatilities which are very close to those of the products sought after, especially

25 of F133a or F123, and some of them are particularly toxic.

F133a and to preexist in the F133a employed as raw material for this second fluorination.

The purification of F123 and, in particular, the removal of its olefinic impurities have been  
5 carried out with the aid of oxidizing agents such as alkali metal permanganates (Patent EP 357 328) or by passing over metal oxides at temperatures which are preferably between 90 and 130°C (Patent EP 370 688) or by treatment with the aid of hydrides and/or strong  
10 bases (Patent EP 493 760).

As with other hydrochlorofluorocarbons, olefinic impurities can be removed from F123 and F124 by catalytic hydrogenation as indicated in Patent Application WO 93/14052.

15 No document is known describing a process for specific purification of F133a and, in particular, removal of olefins present in F133a.

It is known, furthermore, that F133a can be easily chlorinated to give F123 and F113a ( $\text{CF}_3\text{CCl}_3$ ).  
20 Such chlorinations can be carried out using thermal initiation in the presence or in the absence of catalysts (Patents EP 526 908 and US 4 145 368) and using photochemical initiation (Patents US 4 060 469 and EP 407 989). These photochemical chlorinations,  
25 which can be carried out equally well in the gas phase (US Patent 4 060 469) and in the liquid phase (Patent

and  $C_4F_6Cl_2$ , some of which are very difficult to separate by distillation from the product to be purified.

In order to be able to remove substantially  
5 all the undesirable olefinic impurities a molar ratio: chlorine/olefinic impurities of between 0.75 and 20, preferably between 0.9 and 1.5, is suitably employed. The optimum value of this ratio depends on the initial concentration of olefins and on the desired degree of  
10 purification.

The photochemical chlorination according to the invention can be carried out in the gas phase or in the liquid phase. "Liquid phase" is here intended to mean either a liquid under autogenous pressure or a  
15 solution in a solvent which is transparent to the radiation employed and inert to chlorination, such as, for example, carbon tetrachloride or trifluorotrchloroethane.

On account of the boiling points of F133a  
20 ( $6.1^\circ C$ ), of F123 ( $27^\circ C$ ) and of F124 ( $-12^\circ C$ ), the photochlorination can be carried out in the liquid phase at atmospheric pressure by cooling the crude hydrochlorofluoroethane to be purified, sufficiently to keep it in the liquid state. It is preferable, however,  
25 to operate at a slight pressure, so as to be able to perform the chlorination at ambient temperature without excessive cooling and to avoid any loss of products by

olefinic compounds. The quantities and the nature of these compounds depend essentially on the conditions in which the hydrochlorofluoroethane was obtained and on the various treatments (for example distillation)

5 carried out on the crude product before the photochlorination stage. The main  $C_4$  impurities which may be present in the F133a or the F123 and which can be removed by the process according to the invention are - without any limitation being implied -

10 fluorinated butenes such as  $CF_3CH=CHCF_3$ ,  $CF_3CCl=CHCF_3$  and  $CF_3CF=CHCF_3$ . The process also makes it possible to remove other olefins, such as  $CF_2=CFCl$ ,  $CF_2=CCl_2$ ,  $CCl_2=CFCl$ , F1122 ( $CHCl=CF_2$ ) and partially fluorinated propenes ( $CF_3CH=CH_2$ ,  $CF_3CF=CH_2$ ,  $CF_3CH=CHF$ ,  $CF_3CF=CHF$  and

15  $CF_3CH=CF_2$ ). As mentioned above, the removal of  $C_4$  olefins is particularly important for, because of their physical and chemical properties,  $C_4$  olefins are difficult to separate from F133a or from F123 by other purification techniques. In the case of F124 the

20 impurities tend to be  $C_2$  or  $C_3$  olefins like F1122 and the abovementioned partially fluorinated propenes.

The materials to be purified may contain from a few tens of ppm to several parts per hundred of  $C_4$  olefinic compounds. The purification process which is

25 the subject-matter of the present invention makes it possible substantially completely to remove these olefins, as well as other olefins that may be present

47 mm internal diameter; downstream it was coupled to a condenser maintained at the temperature of 10°C, followed by a sampling point. Upstream there was a mixing chamber, a chlorine gas entry and a peristaltic pump continuously delivering the solution to be treated; the chlorine flow rate was adjusted with the aid of a mass flowmeter to the flow rate of the solution and to its olefin concentration.

The light source consisted of a Heraeus TQ 150 high-pressure mercury vapour lamp delivering a radiant power of 16 watts in the 320-500 nm band. The lamp was cooled by a concentric quartz jacket of 38 mm external diameter; the length of the luminous arc was 41 mm.

The coil was fed with a solution in trifluorotrichloroethane (F113) containing 25 % by weight of a crude F133a containing, by weight:

	90.0 %	of	F133a
	9.35 %	of	tr C <sub>4</sub> F <sub>7</sub> H + C <sub>4</sub> F <sub>6</sub> H <sub>2</sub> with 80 %
20			of tr C <sub>4</sub> F <sub>7</sub> H
	0.2 %	of	cis C <sub>4</sub> F <sub>7</sub> H
	0.45 %	of	C <sub>4</sub> F <sub>6</sub> HCl

in which gaseous chlorine was bubbled and dissolved at a flow rate of 3.42 l/h (0.15 mol/h). The flow rate of the solution was 530 ml/h and, in these conditions, the molar ratio Cl<sub>2</sub>/olefins (C<sub>4</sub>F<sub>7</sub>H, C<sub>4</sub>F<sub>6</sub>H<sub>2</sub> and C<sub>4</sub>F<sub>6</sub>HCl) was equal to 1, with a chlorine concentration of

EXAMPLE 2

In a thick-walled Pyrex tube of 12/18 mm diameter was placed a mixture of 6.51 g of pure F133a and 0.487 g of olefins  $C_4F_7H/C_4F_6H_2$  (11.2 mol% of  $tr$   $C_4F_7H$ ), to which 0.24 g of chlorine (3.3 mmol) was added.

The tube was sealed and exposed for 45 minutes to the light emitted by a tubular UV lamp 210 mm in length and 15.5 mm in diameter and with an electrical power of 6 watts, emitting a radiation centred on the 365 nm wavelength. The axis of the tube was placed in parallel to that of the lamp and 40 mm from the latter.

After the test the tube was opened and its content, recovered in a sufficient volume of  $CCl_4$ , was analysed by gas phase chromatography. It was found that 99.3 % of the olefins were removed in the form of  $C_4F_6H_2Cl_2$  and  $C_4F_7HCl_2$ , whereas only 0.60 % of the F133a was converted to F123 (0.54 %) and to F113a (0.06 %).

EXAMPLE 3

The same device as in Example 2 was employed, the F133a being replaced with a sample of F124 still containing 300 ppm of F1122 ( $CF_2=CHCl$ ).

7 g of this sample were placed in a 12-mm internal diameter thick-walled Pyrex tube and 0.5 ml of chlorine gas, measured in standard temperature and pressure conditions, was added using a suitable device.

EXAMPLE 5

Through an annular reactor with a capacity of 100 ml was circulated an impure F133a containing 4 % by weight of the two olefins  $C_4F_7H$  and  $C_4F_6H_2$  and 0.5 % of  $C_4F_6HCl$ . At its centre the apparatus contained a lamp carrier in which a Hanau TQ 150 Z1 photoemitter tube had been placed, the main emission lines of which are at 366, 405, 417 and 436 nm.

The reactor itself consisted of an annular space bounded by two Pyrex tubes 1.8 mm in thickness and 38 and 46.6 mm in diameter respectively; the maximum path of the radiation through the reaction mixture therefore did not exceed 8.6 mm. The working height was 18 cm and the apparatus was designed to withstand a working pressure of 4.5 bars.

The F133a was injected at a flow rate of 550 ml/h with the aid of a metering pump and mixed with a chlorine gas flow rate of 0.31 mol/h. At the exit of the photochlorinator the mixture was cooled to 0°C and analysed by gas phase chromatography. It contained, by weight, 90.91 % of F133a, 0.02 % of  $C_4F_7H/C_4F_6H_2$ , 0.006 % of  $C_4F_6HCl$ , 2.9 % of F123 and 6.1 % of products of chlorination of the olefins ( $C_4F_6H_2Cl_2$ ,  $C_4F_7HCl_2$  and  $C_4F_6HCl_3$ ).

After distillation and removal of the heavy fractions, an F133a with a purity of 99.97 % by weight was finally obtained, containing less than 10 ppm of



The same UV lamp as in Example 2 was placed in the tube-carrier, bounding a working volume of 285 ml between its two electrodes.

With the UV lamp switched on, the reactor was  
5 fed continuously with a 0.57 l/h stream of chlorine and a solution, in carbon tetrachloride, of a mixture of F133a and of olefins  $C_4F_7H/C_4F_6H_2$  (11.2 mol% of  $C_4F_7H$ ) containing, after dilution, 84 g/l of F133a and 5.6 g/l of the two olefins. The flow rate of solution was  
10 adjusted to 0.75 l/h so as to have a chlorine/olefins molar ratio of 0.94.

After equilibration of the chlorine concentration the chromatographic analysis of the solution at the exit of the reactor showed that 83.7 %  
15 of the two olefins had been removed, the loss of F133a being only 0.33 %.

7. Process according to any of Claims 1 to 3, in which the irradiation is performed in the liquid phase at a temperature between 10 and 50°C.

8. Process according to Claim 6 or 7, in which the hydrochlorofluoroethane is in solution in a solvent which is transparent to the radiation employed and inert to chlorination.

9. Process according to Claim 8, in which the solvent is carbon tetrachloride or trichlorotrifluoroethane.

10. Process according to any preceding Claim, in which the light energy is between 5 and 1000 kJ/h/l.

11. Process according to any of Claims 1 to 9, in which the light energy is between 50 and 500 kJ/h/l.

12. Process according to any preceding Claim, in which, after irradiation, the hydrochlorofluoroethane is distilled to separate off the chlorine compounds formed.

13. Process according to any preceding Claim, for the purification of 1-chloro-2,2,2-trifluoroethane.

14. Process according to Claim 1 substantially as described in any one of the Examples.

15. A hydrochlorofluoroethane purified by the process claimed in any preceding Claim.



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**Claims searched:** 1-16

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**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

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Other: Data-Base: Cas-on-line

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
	No Relevant Document	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.